

PATENT SPECIFICATION

(11) 1 458 561

1 458 561

- (21) Application No. 10261/74 (22) Filed 7 March 1974
 (44) Complete Specification published 15 Dec. 1976
 (51) INT CL² C08L 67/02.
 (52) Index at acceptance
 C3R 3C 3D13 3D2A 3D2E 3D6 3N1 3NZ C11 C12 C13P
 C28X C33B C3R L3A L5B L5X L6D
 (72) Inventors KAZUYA CHIMURA, HIROSHI IWATA,
 TAKASHI KANEKO and RYUICHI NAKAZONO



(54) IMPROVEMENT IN AND RELATING TO POLYESTER FIBERS HAVING EXCELLENT DYEABILITY

(71) We, MITSUBISHI RAYON CO. LIMITED, a corporation organized under the laws of Japan, of 8, Kyobashi-2-chome, chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a method of preparing polyester fibers improved in dyeability and more particularly it relates to a method of preparing polyester fibers having a high dyeability with excellent fiber properties possessed by polyethylene terephthalate fibers. It also relates to fibers made by such methods.

Polyethylene terephthalate fibers have been widely used for various purposes because of their excellent properties, but they have a great defect that they are inferior to other fibers in dyeability where they are used for clothing.

For improving the dyeability of polyethylene terephthalate fibers, various methods have been attempted, e.g., copolymerization, addition of various easily dyeable high molecular weight or low molecular weight materials, and physical modification during the fiber production step. However, using these methods, the excellent mechanical and heat resistant properties of polyethylene terephthalate fibers are damaged, stable production thereof is difficult and the cost of production is increased excessively. Thus, industrially acceptable methods have not yet been established. Therefore, dyeing of polyethylene terephthalate fibers has been carried out mainly by high pressure dyeing or carrier-dyeing methods.

According to this invention we provide a method of preparing dyeable polyester fibers having an initial Young's modulus of at least 70 g/d which comprises obtaining a polymer by melt mixing 60 to 95% by weight of a polyester containing at least 95 mol % of ethylene terephthalate units having an intrinsic viscosity (η) PET of $0.9 \geq (\eta)$ PET ≥ 0.5 and 40 to 5% by weight of a polyester containing at least 85 mole % of tetramethylene terephthalate units having an intrinsic viscosity

(η) PTMT of $1.5 \geq (\eta)$ PTMT ≥ 0.7 , provided that (η) PTMT $\geq (\eta)$ PET + 0.1 to cause an ester interchange reaction therebetween and then spinning the mixtures so that the filamentary polymer (as defined herein) has a melting point T_m ($^{\circ}\text{C}$) of $T_{m0} - 5$ ($^{\circ}\text{C}$) $\geq T_m \geq T_{m0} - 20$ ($^{\circ}\text{C}$) (wherein T_{m0} means the melting point of the polyester containing at least 95 mol % of ethylene terephthalate unit) and a crystallizing temperature of 170°C or higher.

We also provide polyester fibres prepared by the above method.

The most important technical point of the present invention is that PTMT and PET are melt mixed so that they are formed into a filamentary polymer having certain suitable characteristic values, from which fibers are produced.

PTMT fibers have much higher dyeability than PET fibers. However, as is easily understood from the fact that PTMT fibers have a melting point of about 225°C , PTMT fibers have low heat resistance and so that conditions employed for finishing conventional polyester fiber articles cannot be applied to PTMT fibers. Moreover, the initial tensile elasticity (Young's modulus) of PTMT fibers is as low as that of polyamide fibers and hence PTMT fibers do not possess the same quality of feel as conventional polyester fiber articles. The fibers prepared by the method of the present invention, on the other hand retain the excellent properties of PET fibers and also retain the high dyeability of PTMT fibers to a greater degree than would be expected from the mixing ratio of PET and PTMT.

The ability to form stable and homogeneous melts and the retaining of excellent fiber properties are mainly due to the high compatibility of PTMT with PET. Furthermore, the unexpectedly high dyeability attained is largely attributable to ester interchange reactions taking place between PET and PTMT during the melt mixing step. In general, when a second component is added in an attempt to improve the dyeability of PET fibers, such

second component which has high dyeability is finely dispersed as discrete particles within the PET fibers. Thus, ordinarily, the desired effect cannot be attained. However, according to the present invention, such a drawback is not caused and a high dyeability can be obtained.

In order to effectively practise the present invention, PET and PTMT must be melt mixed and spun into fiber so that the melting point and the crystallizing temperature of the filamentary polymer, which is defined as strands or unstretched filaments which have been extruded from a nozzle but have not yet been taken up or wound must satisfy the following formulas:

$$T_{m,-5^{\circ}C} \geq T_m \geq T_{m,-20^{\circ}C} \quad (1)$$

$$T_c \geq 170^{\circ}C \quad (2)$$

(wherein T_m and $T_{m,-}$ are the same as defined before and T_c is the crystallizing temperature of the filamentary polymer).

More preferably,

$$T_{m,-5^{\circ}C} \geq T_m \geq T_{m,-20^{\circ}C}$$

$$T_c \geq 175^{\circ}C$$

(wherein T_m , $T_{m,-}$ and T_c are the same as defined before).

Only when the above mentioned characteristics are imparted to the filamentary polymer, the resulting polyester fibers which are not inferior to PET fibers in thermal and mechanical properties such as heat resistance, heat settability, Young's modulus, and which have markedly improved dyeability can be obtained.

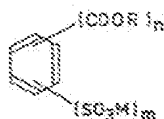
The melting point and crystallizing temperature of the filamentary polymer obtained by melt-mixing and spinning depends greatly upon the formation of a block-copolymer and the shortening of each repeating unit in the block copolymer caused by a partial ester interchange reaction between PET and PTMT. Furthermore, by forming the block copolymer in this way, a deterioration in the fiber properties from those of PET fiber can be decreased and a remarkable improvement in dyeability can be attained.

When T_m of the filamentary polymer obtained by melt-mixing and subsequent spinning exceeds $T_{m,-5^{\circ}C}$, said formation of block copolymer caused by ester interchange reaction hardly proceeds. Therefore, no synergistic effect in improvement in dyeability can be expected. On the other hand, when T_m is lower than $T_{m,-5^{\circ}C}$, the shortening of the repeating unit of the block copolymer becomes excessive. Therefore, although satisfactory dyeability can be obtained, the thermal and

mechanical properties of the fibers such as heat resistance, heat settability of crimps, dimensional stability, and Young's modulus markedly deteriorate and the resultant fibers have fiber properties similar or inferior to those of the ordinary copolymer-type polyester fibers. This result is reflected in the crystallizing temperature T_c . T_c is a characteristic value which is, in a sense, also considered a standard for crystallizing speed. Usually, the crystallizing temperature T_c gradually decreases from the crystallizing temperature of PET (205—210°C) with the progress of the ester interchange reaction between PET and PTMT. That is, the crystallizing speed decreases. Therefore, with a decrease in T_c to below 170°C, the heat resistant property of the fibers greatly deteriorates and also the value of Young's modulus is markedly decreased. As a result, the quality of feel peculiar to PET fiber articles is lost. These characteristics depend on the mixing ratio of PTMT or temperature at melt mixing and spinning steps or retention time at molten state. In order to attain improved dyeability, PTMT must be mixed in an amount of at least 5% by weight preferably at least 10% by weight, in addition to the effect of ester interchange reaction between the two polymers. On the other hand, for ensuring stability in production of fibers and excellence in fiber properties, the mixing proportion of PTMT should be less than 40% by weight, preferably 35% by weight. The PTMT polymer used in the present invention is preferably composed of 100 mol % of tetramethylene terephthalate units, but it may contain up to 15 mol % of other components. The component to be copolymerized with PTMT can be, for instance, polyols such as ethylene glycol, triethylene glycol, 1,4-cyclohexane dimethanol, glycerine, or pentaerythritol, polyether glycols such as polyethylene ether glycol, polypropylene ether glycol, polytetramethylene ether glycol and dicarboxylic acids such as isophthalic acid, 1,4- or 1,5- or 2,6-naphthalic acid, sebacic acid, or adipic acid.

The PET polymer used in the present invention is composed of at least 95 mol % of ethylene terephthalate units for ensuring excellent fiber properties. Another component to be copolymerized with PET can be, for instance, C_2 to C_6 polyhydric alcohols such as triethylene glycol, tetramethylene glycol, cyclohexane dimethanol, glycerol, pentaerythritol, polyether glycols such as polyethylene ether glycol, polypropylene ether glycol, or polytetramethylene ether glycol, and dicarboxylic acids such as isophthalic acid, 1,4- or 1,5- or 2,6-naphthalic acid, sebacic acid, or adipic acid.

As the dicarboxylic acid component, a sulfonate compound represented by the formula:



(wherein R is hydrogen, a C_1 to C_6 alkyl or a hydroxyalkyl radical, M is an alkali metal, m is 1 or 2 and n is 1, 2 or 3) may be copolymerized with PET for especially imparting to the PET affinity to a basic dye.

It is known to copolymerize merely the sulfonate compound with PET to obtain polyester fibers dyeable with a basic dye, but such method is still not satisfactory for ensuring effective utilization of dye site and dyeing procedure. According to the present invention, PET or PTMT with which a sulfonate compound is copolymerized is used to attain effective utilization of dye sites, to make it possible to stably produce the fibers, to impart to the fibers sufficiently good fiber properties and to give the fibers a high dyeability with a simple dyeing procedure at a temperature lower than 100°C at normal pressure. Thus, the present invention can provide a method of preparing basic dye-dyeable polyester fibers having the above characteristics.

Preferably, said sulfonate compound is copolymerized in a proportion of not more than 2.2 mol % based on the polyethylene terephthalate and in a proportion of not more than 10 mol %, based on the polytetramethylene terephthalate to ensure the desired melting characteristic of the resultant polymer. Furthermore, for increasing heat and oxidation resistance of the polymer, it is effective to add an additive in an amount of 0.01 to 2.0% by weight of the resultant polymer during the polymerization of the PET and PTMT or during the melt mixing of the PET and PTMT. Suitable heat and oxidation resisting additives are, for instance: phosphorous esters such as triphenyl phosphite, tris(p-nonylphenyl)phosphite, and trimethyl phosphite, and hindered phenol compounds such as

di-tert-butyl-p-cresol,
2,2 - methylene - bis(4 - methyl - 6 - tert-butylphenol),
2,2 - thio - bis(4 - methyl - 6 - tert-butylphenol),
tetrakis[3 - (4 - hydroxy - 3,5 - di - tert-butylphenyl) - propionyl oxymethyl]-methane,
2,6 - bis(4 - hydroxy - 3,5 - di - tert-butylphenoxy)-6-ocryl-thio-S-triazine,
1,6 - hexamethylene - bis(β - 4 - hydroxy-3,5-di-tert-butylphenylpropion)amide,
4 - hydroxy - 3,5 - di - tert - butylphenylphosphite,
4 - hydroxy - 3,5 - di - tert - butylphenylphosphate,
diethyl - 4 - hydroxy - 3,5 - di - tert - butylbenzyl phosphate.

The polyester comprising at least 95 mol % of ethylene terephthalate units used in the present invention can be prepared in accordance with the known methods, e.g., the method disclosed in Japanese Patent Publication No. 8594/56 and the method disclosed in "Polyester Fasern" (Akademie Verlag Berlin 1965).

The polyester comprising at least 85 mol % of tetramethylene terephthalate units can be prepared in accordance with the method disclosed, for example, in Japanese Patent Publication (OPI which means "open to public inspection") No. 5749/71 and "Journal of Polymer Science" (A-1 4 1851 1966).

The ester interchange reaction between PET and PTMT in the present invention may be carried out by various methods. For example, separately polymerized PET and PTMT are mixed in a kettle, the resultant mixture is extruded to form chips and the chips are melt spun; or PET and PTMT which are separately molded into chips are fed to two extruders, respectively, the molten polymers are introduced into one mixer and the polymers are spun while carrying out melt mixing and proper ester interchange reaction; or more simply, PET and PTMT which are molded into chips are fed into one extruder in finely ground form or as they are, in which ester interchange reaction is carried out while melt mixing the two and the mixture is spun. Control of the ester interchange reaction may be accomplished by suitably setting mixing ratio, melting temperature and melt mixing time.

The mixing proportion of PTMT to PET is 5 to 40%, preferably 15 to 35% by weight in view of the properties of the fibers obtained.

The melt mixing temperature and time may be suitably selected within the ranges of 265 to 300°C and 3 to 120 minutes so that melting point and crystallizing temperature of the filamentary polyester obtained satisfy the formulas (1) and (2) mentioned before. It is generally preferred that when the melt mixing time is long, the temperature is set low and when the mixing ratio of PTMT is high, the melting time is set short and the temperature is set low.

In order to stably and effectively practice the present invention, the polymerization degree of the PET and PTMT which may conveniently be estimated by their viscosity in solution, must be suitably selected. For controlling production conditions and ensuring excellent fiber properties, the intrinsic viscosities of PET and PTMT, $[\eta]$ PET and $[\eta]$ PTMT must be $0.9 \geq [\eta]$ PET ≥ 0.5 and $1.5 \geq [\eta]$ PTMT ≥ 0.7 , respectively. Furthermore, in order to ensure processability during the melt mixing and spinning steps, the intrinsic viscosities of the two polymers must satisfy the equations $[\eta]$ PTMT $\geq [\eta]$ PET + 0.1. This is the effective means for attaining homogeneous disper-

sion and mixing of the two components.

The molten polymers may be made into fibers in accordance with the usual process for producing polyethylene terephthalate fibers. Especially, in the present invention, the spinning temperature may be lowered to 10—15° C lower than the spinning temperature usually employed for spinning of the conventional polyester fibers and a preferred spinning temperature may be selected within the range of 256° C to 290° C.

Furthermore, the fibers prepared by the method of the present invention may be drawn at a temperature which is 10° C—20° C lower than that for the conventional polyester fibers at a drawing ratio of 2—6 times, preferably 2.5—4 times to accomplish stable drawing without causing fluffing, breakage, or whitening phenomena.

For further improving dyeability, the polyester fibers prepared by the method of the present invention may be made into drawn fibers low in crystallinity and orientation by drawing them at a temperature lower than 100° C, preferably lower than 85° C which is lower than the drawing temperature usually employed.

The polyester fibers prepared by the method of the present invention have a high dyeability and moreover, when copolymerized with a sulfonate compound, they have higher dyeability as compared with the known sulfonate-copolymerized polyester fibers and are also excellent in color fastness.

The other benefit of the present invention is that the dyeability is markedly improved while excellent fiber properties are retained. For example, the initial Young's modulus which is an important characteristic of polyester fibers is at least 70 g/denier, usually at least 80 g/denier which confers excellent hand on woven and knitted fabrics made from the fibers.

Measurements of characteristic values in the present invention were effected as follows:

(1) Mechanical characteristics:

Strength, ultimate elongation and initial Young's modulus were measured in accordance with JIS 1070—5.

Measuring atmosphere	20° C, 65% RH
Length of sample	20 cm
Extension velocity	10 cm/min

The initial Young's modulus was calculated as stress (g/denier) at 100% elongation from gradient of elongation stress curve in the initial elongation area.

(2) Measurement of melting point and crystallizing temperature:

Differential Scanning Calorimeter (DSC—

1) manufactured by Perkin-Elmer Corpora-

tion was used. Amount of sample (filamentary polymer) was about 5—10 mg.

Melting point (T_m and T_{m0}):

This was expressed by peak temperature of endothermic curve appearing at an elevation rate of 10° C/min.

Crystallizing temperature (T_c):

After the polymer was molten, the molten polymer was kept at $T_m + 10^\circ$ C for 5 minutes and thereafter it was cooled at 10° C/min. The crystallizing temperature was expressed by peak temperature of exothermic curve for crystallization which appeared at said cooling.

The measurement of the melting point and crystallizing temperature was effected in nitrogen stream.

(3) Measurement of intrinsic viscosity $[\eta]$:

Intrinsic viscosity was measured at 25° C with use of a mixed solvent of tetrachloroethylene and phenol (50/50 in weight ratio).

(4) Heat resistance:

When the fiber was texturized with changing the false-twisting temperature by a model false twister, temperature at which incomplete untwisting (impossible to false-twist) began was taken as maximum temperature of heat resistance of the fibers. The test was carried out under the following conditions: texturizing speed . . . about 10 m/min; the number of false twists

$$\frac{275000}{D+60} + 800$$

(See Japanese Patent Publication No. 5996/56; "D" means denier); and length of hot plate . . . 30 cm.

(5) Heat settability:

The lengths L_0 and l of texturized yarn before and after subjected to boiling water treatment, respectively under load of 0.2 gram/d were measured. The settability was expressed by shrinkage

$$\frac{L_0 - l}{L_0} \times 100$$

at the boiling water treatment.

Said boiling water treatment was carried out for 20 minutes.

(6) Dyeing method and evaluation of dyeability:

Unless specifically stated, dyeing method and measurement of dye exhaustion in Examples hereinafter given are as follows:

(In case of disperse dye).

Sample was subjected to scouring with an aqueous solution containing 0.5 g/l of monononyl phenyl ether of polyoxyethylene at a liquor ratio of 1:50 at 70° C for 20 minutes and then was dyed with 5% owf blue disperse dye (CI60767) and 3% owf formalin condensation product of sodium naphthalene-sulfonate at a pH of 3—4, at a liquor ratio of 1:50 at 100° C for 60 minutes. Thus dyed product was washed with water and then soaped with an aqueous solution of 1 g/l of soda ash and 1 g/l of monononylphenyl ether of polyoxyethylene at a liquor ratio of 1:50 and at 85° C for 20 minutes.

Dye exhaustion was measured as follows: 100 mg of the dyed yarns or fabric was subjected to dye-extraction with 100 ml of a mixed solution of 49 volume % of N,N' -dimethylformamide, 50 volume % of ethylene glycol and 1 volume % of acetic acid at 150° C. Light absorbances of the extract and dye solution having a known concentration were measured and dye-exhaustion was calculated.

(In case of a cationic dye).

A sample was scoured in the same manner as in case of the disperse dye and then was dyed with 5% owf blue cationic dye (CI42025) at a pH of 3—4, a liquor ratio of 1:50, at 100° C for 60 minutes. Then, the dyed sample was washed with water and then was subjected to soaping under the same conditions as in case of the disperse dye.

Dye exhaustion (%) was colorimetrically measured on residual solution by diffraction grating type Spectronic 20 manufactured by Shimadzu Seisakusho K.K. (Spectronic 20 is a Trade Mark).

The following Examples illustrate the invention.

Example 1.

This Example illustrates the importance of the polyethylene terephthalate/tetramethylene terephthalate mixing ratio.

Polyethylene terephthalate having $[\eta]$ of 0.71 was prepared in accordance with the usual method using manganous acetate and germanium dioxide as a catalyst. To 100 parts of dimethyl terephthalate and 73 parts of ethylene glycol was added 0.03 part of manganous acetate and ester interchange reaction was allowed to take place with elevation of temperature to 240° C. Then, 0.05 part of triphenylphosphite and 0.03 part of germanium dioxide dissolved in ethylene glycol were added thereto and temperature was elevated to 285° C, at which condensation polymerization was carried out for 2 hours under a reduced pressure of 1 mmHg. After polymerization reached a given degree, pressure was applied thereto with nitrogen gas and the melt was taken out, cooled in water and molded into chips. In addition, to 100 parts of di-

methyl terephthalate and 74 parts of 1,4-butanediol was added 0.034 part of hexa-acetoxyditanoxane and ester interchange was carried out while temperature was gradually elevated to 200° C. Then, the temperature was elevated to 250° C, at which condensation polymerization was carried out under a reduced pressure of 1—2 mmHg for about 2.5 hours to obtain polytetramethylene terephthalate having $[\eta]$ of 1.03.

Melting point and crystallizing temperature of polymer chips of polyethylene terephthalate were 260° C and 207° C, respectively and those of polytetramethylene terephthalate were 225° C and 190° C, respectively.

These polymer chips were subjected to drying treatment with vacuum drier at 150° C and while they were mixed in the following weight ratio of polyethylene terephthalate/polytetramethylene terephthalate: (A) 90/10, (B) 80/20, (C) 70/30 and (D) for comparison 57/43, they were fed to an extruder and melt mixed at 295° C. The mixture was continuously fed to a spinning head set at 287° C and spun therefrom and taken up to obtain undrawn filaments of 240 d/36 f. Residence time of the mixture in the extruder was about 6 minutes and residence time in the spinning head was about 9 minutes. Melting point and crystallization temperature of the filamentary polymer (strand collected without winding) are enumerated in Table 1. Melting point of polymer chips obtained by condensation polymerization of polyethylene/tetramethylene terephthalate copolymer having the same proportions as mixing ratio of the corresponding samples is also shown in Table 1. The melting point of the filamentary polymer gradually decreased with increase in proportion of polytetramethylene terephthalate, but was still higher than that of the corresponding copolymers. This fact indicates that the filamentary polymer compositions in the present invention were not divided into units by ester interchange reaction but remained as block copolymers in which the lengths of the sequences of each component were considerable.

The undrawn filaments of 234 d/36 f were drawn at a draw ratio of 3.3 times with a pin at 85° C and a hot plate at 150° C to obtain drawn filaments of 72 d/36 f.

Dyeabilities, mechanical characteristics (strength, elongation, initial Young's modulus), heat resistant characteristics of the drawn filaments and shrinkage in boiling water of crimped yarns are also shown in Table 1. The polyethylene terephthalate fibers used in the comparative Example are those obtained by melt spinning the polyethylene terephthalate chips prepared in this Example at 287° C to obtain undrawn filaments of 235 d/36 f and drawing the undrawn filaments at drawing ratio of 3.26 times under the same conditions as in this Example. Furthermore, the texturiz-

ing temperature was 210° C in case of the comparative polyethylene terephthalate fibers and samples (A) and (B), 200° C in case of sample (C) and 178° C in case of sample (D).

As is clear from these results, samples (A), (B) and (C) according to the present invention had excellent dyeability, fiber properties, heat resistance, and dimension stability while sample (D) which contained polytetramethylene terephthalate in a larger proportion had excellent dyeability, but considerably lower fiber properties, heat resistance and dimension stability.

Comparative Example 1.

This comparative Example relates to heat history of the mixed composition.

A mixture of polyethylene terephthalate and polytetramethylene terephthalate used in Example 1 in a weight ratio of 83:17 was melt

mixed and spun through extruder and spinning head set at 275° C to obtain undrawn filaments of 235 d/36 f. Residence time in the extruder was about 2.5 minutes and that in the spinning head was about 3 minutes. The filamentary polymer which was not taken up had a melting point of 257° C and a crystallizing temperature of 200° C.

The undrawn filaments were drawn in the same manner as in Example 1 to obtain drawn filaments of 72 d/36 f. The characteristic values thereof are also shown in Table 1.

The mechanical properties and heat resistance of the sample (E) of comparative Example 1 were satisfactory but the dyeability was inferior to sample (A). Thus, when the filamentary polymer had its melting point outside the specified range ($T_{m, -3^{\circ}C} \geq T_m \geq T_{m, +20^{\circ}C}$) the desired excellent dyeability cannot be attained.

TABLE I

Sample	Characteristics of filamentary polymer		Dye exhaustion (%)	Mechanical characteristics			Heat resistance (°C)	Settability (shrinkage in boiling water) (%)	Melting point of copolymer (for reference) (°C)
	Melting point (°C)	Crystallizing temperature (°C)		Strength (g/d)	Elongation (%)	Young's modulus (g/d)			
A PET/PTMT = 90/10	254	202	69	5.1	25	95	225	2.5	(ET/TMT = 90/10) 240
B PET/PTMT = 80/20	251	194	73	5.0	28	87	218	2.7	(ET/TMT = 80/20) 220
C PET/PTMT = 70/30	247	185	75	4.8	28	80	205	3.2	(ET/TMT = 70/30) 201
D PET/PTMT = 57/43	237	174	83	4.2	31	64	185	5.5	—
Polyethylene terephthalate	260	207	17	5.2	25	101	228	2.3	—
E PET/PTMT = 83/17	257	200	42	5.1	28	92	220	2.5	—

PET: Polyethylene terephthalate

PTMT: Polytetramethylene terephthalate

Example 2.

The same polyethylene terephthalate chips and polytetramethylene terephthalate chips as used in Example 1 were mixed in a weight ratio of 65:35 with V type blender. The mixture was dried in vacuo at 130° C for 5 hours and then was melt spun through an extruder at 280° C and at a spinning temperature of 275° C to obtain undrawn filaments, which were drawn under the same conditions

as in Example 1 to obtain drawn filaments (F) of 72 d/24 f. Residence time in the extruder and that in the spinning head were 3 minutes and 5 minutes, respectively. On the other hand, mixed chips of the same composition as above were melt mixed through an extruder at 295° C and spun at a spinning temperature of 290° C. The resultant undrawn filaments were drawn under the same conditions as in Example 1 to obtain drawn filaments (G) of 72

15

20

10

reaction had proceeded to such an extent that melting point and crystallizing temperature were outside the ranges specified in the present invention were poor so that in these respects the fiber no longer retained the characteristics of polyester fibers. On the other hand, sample (F) of the present invention had excellent mechanical properties as well as dyeability.

15

d/24 f. Residence time in the extruder and that in the spinning head were 8 minutes and 12 minutes, respectively. Characteristics of the filamentary polymer and fiber characteristics of the samples (F) and (G) are shown in Table 2.

5

From this Example, it is recognized the mechanical properties and heat resistance of the sample (G) in which ester interchange

TABLE 2

Sample	Characteristics of filamentary polymer		Dye exhaustion	Mechanical characteristics			Heat resistance
	Melting point	Crystallizing temperature		Strength	Elongation	Young's modulus	
F (present invention)	249°C	184°C	78%	4.7 g/d	26%	82 g/d	203°C
G (comparative)	237°C	176°C	82%	4.0 g/d	35%	70 g/d	182°C

Example 3.

Undrawn filaments obtained in Example 1 which correspond to sample (B) (polytetramethylene terephthalate 20%) were drawn using feed rolls heated to 70° C to obtain drawn filaments of 72 d/36 f without heat set treatment by a hot plate. The drawn filaments thus obtained showed a dye exhaustion of 82% with a disperse dye at 100° C which was higher than that of the corresponding sample (B). Furthermore, they had a strength of 4.5 g/d and a Young's modulus of 82 g/d and thus retained sufficient properties of polyester fibers.

20

25

30

As is clear from the above results, when the fibers of the present invention were drawn at a low temperature, dyeability and fiber properties were further improved.

Example 4.

After completion of polymerization of polytetramethylene terephthalate in the same manner as in Example 1, 1,6-hexamethylene-bis-(β , 4 - hydroxy - 3,5 - di - tert - butylphenyl)propanamide was added in an amount of 0.1% by weight of the polytetramethylene terephthalate into the vessel in nitrogen gas under atmospheric pressure and then they

40

45

were mixed with agitation at 250° C for 10 minutes. Then, the resultant polymer was taken out. This polymer had a $[\eta]$ of 1.01. Thirty parts of this polytetramethylene terephthalate and 70 parts of polyethylene terephthalate which had a $[\eta]$ of 0.71 and which was prepared in accordance with the usual method using calcium acetate, together with antimony trioxide as a catalyst and trimethyl phosphate as a stabilizer were melt mixed and spun using the same spinning machine as in Example 1 at a melt mixing temperature of 290° C and at a spinning temperature of 290° C. Residence time of the mixture in the extruder and spinning head were 5 minutes and 9 minutes respectively. The resultant filaments were drawn at 90° C and heat treatment at 160° C to obtain filaments of 50 d/24 f. The fibers had an initial Young's modulus of 80 g/d. Melting point of the filamentary polymer was 245° C and crystallizing temperature was 182° C.

The spinning was continued for 48 hours. One hundred pairs of drawn filaments in an amount of 1 kg on each pair were prepared from said undrawn filaments, but substantially no breakage, occurred and the resultant fibers on each pair had no defects such as fluffs or loops.

For comparison, fibers were produced in the same manner as mentioned above except that polytetramethylene terephthalate to which no 1,6-hexamethylene-bis(β -4-hydroxy-3,5-di-tert-butyl-phenylpropion)amide was added was used. In this case, after a lapse of about 8 hours from the beginning of spinning, black material adhered to the circumference of the spinning holes of the nozzle, which resulted in a deformation of the spun filaments, and this defect became more conspicuous with lapse of time. When the thus obtained undrawn filaments were drawn, those which were obtained within a short time from the beginning of spinning showed no troubles, but those which were obtained after about 8 hours, caused considerable winding at drawing and furthermore those which were obtained after more than about 8 hours showed breakage. The fibers obtained had much fluffs and loops. As is clear from this Example, the fibers obtained from a polymer blend containing an antioxidant had excellent spinning stability and drawing stability.

Example 5.

Example 4 was repeated except that 0.2% by weight of tris(p-nonylphenyl)phosphite was substituted for 1,6-hexamethylene-bis(β -4-hydroxy-3,5-di-tert-butyl-phenylpropion)amide to obtain substantially the same excellent results as those obtained in Example 4.

Example 6.

Eighty parts of polyethylene terephthalate which had $[\eta]$ of 0.71 and which was prepared

by the usual method using manganous acetate and germanium dioxide as catalyst and triphenyl phosphite as a stabilizer and 20 parts of polytetramethylene terephthalate having a $[\eta]$ of 1.03 were melt-mixed at 295° C and spun at 290° C. Residence time in the extruder and that in spinning head were 5 minutes and 9 minutes respectively. The resultant filaments were drawn to 3.3 times at 600 m/min using a pin at 90° C and a hot plate at 160° C to obtain fibers of 50 d/24 f. The fibers had an initial Young's modulus of 88 g/d. Melting point and crystallizing temperature of the filamentary polymer were 250° C and 194° C, respectively. In this case, defects were recognized in spinning and drawing stabilities as in Example 4, but these were small enough to be ignored. On the other hand, the above procedure of this Example was repeated except that polyethylene terephthalate having a $[\eta]$ of 0.70 which was prepared in the same manner as above except that triphenyl phosphite was substituted for triphenyl phosphite as a stabilizer was employed. During the spinning, kneeling occurred and winding and breakage considerably occurred at drawing. Thus, the fibers obtained had defects such as fluffs and loops.

As is clear from this Example, in case of practicing the present invention with use of polyethylene terephthalate prepared using phosphorous acid triester compound as a stabilizer, the fibers obtained had superior spinning and drawing stabilities than those in case of using polyethylene terephthalate prepared using a phosphoric acid triester compound as a stabilizer.

Example 7.

A copolymerized polyester having a $[\eta]$ of 0.53 and a melting point of 251° C was obtained by the usual method from 1.7 part of sodium 3,5-di(carbomethoxy)benzene sulfonate (2.2 mol % based on polyethylene terephthalate), 49 parts of dimethyl terephthalate, 33.8 parts of ethylene glycol, 0.04 part of sodium methoxide, 0.023 part of manganous acetate and 0.015 part of antimony trioxide. Ninety parts of said polymer and 10 parts of polytetramethylene terephthalate having a $[\eta]$ of 0.98 were mixed and spun through extruder at 295° C and spinning head at 280° C. Residence time in the extruder and that in spinning head were 6 minutes respectively. The resultant filaments were drawn at a drawing ratio of 3.3 times at 600 m/min using a pin of 90° C and a hot plate of 150° C to obtain fibers of 150 d/30 f. The fibers had an initial Young's modulus of 85 g/d. Melting point of the filamentary polymer was 246° C and crystallizing temperature was 177° C. Said fibers were dyed with 5% owf blue cationic dye (CI42025) at a pH of 3, at 100° C for 60 minutes. Dye exhaustion was

75%. On the other hand, the above procedure was repeated except that only said copolymerized polyester was used. In this case, dye exhaustion was 38%. From these results, it was recognized that the fibers of the present invention had excellent dyeability.

Example 8.

Copolymerized polyethylene terephthalates and polytetramethylene terephthalates with which sodium 3,5-di(carbomethyl)benzene sulfonate was copolymerized as a third component were prepared as shown in Table 3.

TABLE 3

Polymer No.	Basic component	Amount of SSI, based on the PET or PTMT (mol %)	$[\eta]$	Melting point (°C)
A	PET	0	0.72	260
B	PTMT	0	1.02	225
C	PET	2.0	0.55	252
D	PET	2.0	0.65	253
E	PTMT	6.6	0.82	203

Note: "SSI" stands for sodium 3,5 di(carbomethoxy) benzene sulfonate.

"DMT" stands for dimethyl terephthalate.

Note: "SSI" stands for sodium 3,5 di(carbomethoxy) benzene sulfonate.

"DMT" stands for dimethyl terephthalate.

Polymer No. D was prepared by solid polymerization of chips of polymer No. C prepared by melt polymerization, at 210° C for 5 hours in vacuo.

Fibers of 150 d/30 f were produced from mixed polymers of polymers No. A, B, C, D and E as shown in Table 4.

Mixing conditions of each polymer were as follows:

The polymers were fed to extruder and melt mixed in it at 295° C. The mixtures were fed to the spinning head. Temperature of head were shown in Table 4. Residence time of the mixture in the extruder and that in the spinning head were 6 minutes and 9 minutes respectively.

respectively.

Spinning conditions for production of fibers were as follows: caliber of nozzle . . . 100 mm; Diameter of holes of nozzle . . . 0.3 mm; The number of hole . . . 30; Filters . . . three 400 mesh stainless steel wire gauze and two 50 mesh stainless steel wire gauze; Extruding amount . . . 60 g/min; Take-up speed . . . 1000 m/min; Spinning temperature . . . as shown in Table 4; Drawing . . . with a pin of 90° C and a hot plate of 160° C, 3.3 times, 600 m/min.

Pressure before the filter at spinning, $[\eta]$ and strength of the resultant fibers and dye exhaustion when dyed under the same conditions as in Example 1 are shown in Table 4.

TABLE 4

Fibers No.	Mixing ratio of polymers	Content of SSI based on the filamentary polymer per (mol %)	Spinning temperature (°C)	Pressure before nozzle (kg/cm ²)	Melting point of filamentary polymer (°C)	Crystallizing temperature of filamentary polymer (°C)	$[\eta]$	Strength (g/d)	Dye exhaustion (%)	Initial Young's Modulus (g/d)
I (Comparative example)	D: 100%	2.0	300	100	253	183	0.55	3.8	31	92
II	D: 90% B: 10%	1.8	290	92	244	175	0.61	4.3	67	86
III (Comparative example)	C: 100%	2.0	285	85	252	183	0.50	3.5	35	90
IV	A: 70% E: 30%	2.0	290	90	240	171	0.68	4.6	72	78

As is clear from Table 4, fibers No. II and IV of the present invention were superior to fibers No. I and III in strength and dyeability.

Example 9.

This example is for showing that excellent articles can be produced from the fibers of the present invention.

(1) The fibers (sample C) obtained in Example 1 were made into texturized yarns (sample C') with a twist number of 3520 T/M. Said texturized yarns C' and other texturized yarns having 75 d/36 f made from ordinary polyethylene terephthalate fibers T were knitted so that the interval between stripes was 10 mm, to obtain a striped knitted

fabric. This fabric was scoured with an aqueous solution containing 0.5% of monononylphenyl ether of polyoxyethylene at 70° C and then was dyed with 5% owf blue disperse dye (CI60767) at 100° C for 60 minutes. Furthermore, the fabric was soaped with an aqueous solution containing a small amount of sodium carbonate and monononylphenyl ether of polyoxyethylene at 85° C for 20 minutes at 85° C to obtain a striped knitted fabric in which the portions of yarns C' showed deep blue color and those of yarns T showed very pale blue color.

(2) The fibers (sample C) produced in Example 1 and polyethylene terephthalate fibers of 75 d/36 f were simultaneously tex-

20

25

30

texturized at 210° C with an texturizing machine to obtain texturized yarns of twist number 2280 T/M. The resultant yarns were knitted into a knitted fabric, which was dyed under the same conditions as in the above (1) to obtain a blue knitted fabric having light and dark portions.

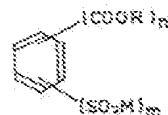
(3) The texturized yarns C' obtained in the above (1) were knitted into a knitted fabric, which was dyed with 3% owl yellow disperse dye (CI26090) at 100° C for 60 minutes. Thereafter, said fabric was sized with a white discharging agent comprising 21% of Maypro gum, 15% of Zn(OH)(HSO₃)CH₂O and 15% of water with use of a printing stand for circular patterns at 130° C for 30 minutes. The fabric was then washed with water and furthermore subjected to reduction soaping with an aqueous solution of 2 g/l of sodium hydroxide, 2 g/l of hydrosulfite and 2 g/l of monononylphenyl ether of polyoxyethylene at a liquor ratio of 1:50 at 85° C for 20 minutes to obtain a knitted fabric where only the circular pattern portions were completely bleached to white, the background remaining yellow.

On the other hand, a knitted fabric made from the ordinary polyethylene terephthalate texturized yarns was dyed with 3% owl yellow disperse dye (CI26070) at 120° C for 60 minutes and then was subjected to white discharge as mentioned above to obtain the fabric in which the circular pattern portions were hardly decolorized and the difference in color between the background part and the circular pattern portions was small.

WHAT WE CLAIM IS:—

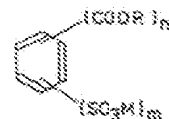
1. A method of preparing dyeable polyester fibers having an initial Young's modulus of at least 70 g/d which comprises obtaining a polymer by melt mixing 60 to 95% by weight of a polyester containing at least 95 mol % of ethylene terephthalate units having an intrinsic viscosity $[\eta]$ PET of $0.9 \geq [\eta]$ PET ≥ 0.5 and 40 to 5% by weight of a polyester containing at least 85 mole % of tetramethylene terephthalate units having an intrinsic viscosity $[\eta]$ PTMT of $1.5 \geq [\eta]$ PTMT ≥ 0.7 , provided that $[\eta]$ PTMT $\geq [\eta]$ PET + 0.1 to cause an ester interchange reaction therebetween and then spinning the mixture, so that the filamentary polymer (as defined herein) has a melting point T_m (°C) of $T_{m, \text{PET}} - 5$ (°C) $\geq T_m \geq T_{m, \text{PTMT}} - 20$ (°C) (wherein $T_{m, \text{PET}}$ means the melting point of the polyester containing at least 95 mol % of ethylene terephthalate unit) and a crystallizing temperature of 170° C or higher.

2. A method according to Claim 1, wherein said polyethylene terephthalate contains not more than 2.2 mol % per polyethylene terephthalate of a sulfonate compound represented by the formula:



(wherein R is selected from hydrogen, C₁ to C₆ alkyl and hydroxy alkyl radicals, M is an alkali metal and m is 1 or 2 and n is 1, 2 or 3) as a dicarboxylic acid component.

3. A method according to claim 1, wherein said polytetramethylene terephthalate contains not more than 10 mol % based on the polytetramethylene terephthalate of a sulfonate compound represented by the formula:



(wherein R is selected from hydrogen, C₁ to C₆ alkyl and hydroxyalkyl radicals, M is an alkali metal, m is 1 or 2 and n is 1, 2 or 3) as a dicarboxylic acid component.

4. A method according to Claim 1, in which there is incorporated into the polyester fibers as heat and oxidation stabilizer, at least one of the following compounds:

triphenyl phosphite,
tris(p-nonylphenyl)phosphite,
trimethyl phosphite,
di-tert-butyl-p-cresol,
2,2 - methylene - bis(4 - methyl - 6 - tert-butylphenol),
2,2-thio-bis(4-methyl-6-tert-butylphenol),
tetrakis[3 - (4 - hydroxy - 3,5 - di - tert-butylphenyl) - propionyl oxymethyl] - methane,
2,6 - bis(4 - hydroxy - 3,5 - di - tert-butylphenoxy) - 6-octyl-thio-S-triazine,
1,6 - hexamethylene - bis(β - 4 - hydroxy - 3,5-di-tert-butylphenylpropion)amide,
4 - hydroxy - 3,5 - di - tert - butylphenyl-phosphite,
4 - hydroxy - 3,5 - di - tert - butylphenyl-phosphate,
diethyl - 4 - hydroxy - 3,5 - di - tert - butylbenzyl phosphate.

5. A method according to Claim 1, wherein the ester interchange reaction is effected by melt mixing the two polyesters at a temperature of 265 to 300° C for 3 to 120 minutes.

6. A method according to Claim 1, in which the polyester fibers are drawn at a drawing temperature of not higher than 100° C.

7. A method according to Claim 1, in which the polymer is obtained by ester inter-

- change reaction of 65 to 85% by weight of polyethylene terephthalate and 35 to 15% by weight of polytetramethylene terephthalate and the filamentary polymer has a crystallizing temperature of 175° C or higher.
- 5 8. Polyester fibers obtained by the method of any preceding Claim.

WITHERS & ROGERS,
Chartered Patent Agents,
148—150, Holborn,
London, EC1N 2NT,
Agents for the Applicant.

Printed for Her Majesty's Stationary Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

